

Polybrominated diphenyl ethers (PBDEs) in English freshwater lakes, 2008-2012

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Submission of research article: “Polybrominated diphenyl ethers (PBDEs) in English freshwater lakes, 2008-2012” by Congqiao Yang, et al.

To whom it may concern

I hereby submit the above paper for consideration as a research article in *Chemosphere*. This is an original piece of work conducted by Congqiao Yang, Stuart Harrad, Mohamed Abou-Elwafa Abdallah, Jennifer Desborough, Neil L. Rose, Simon D. Turner, Thomas A. Davidson, and Ben Goldsmith (see below the details for all authors). The current study presents an investigation of the temporal/seasonal trends and spatial distribution of the concentrations of tri to hexa-BDEs in water from 9 freshwater lakes throughout England from April 2008 to February 2012. We believe that it warrants publication in *Chemosphere* as this study is only the second report – and the most comprehensive to date - of concentrations of PBDEs in European lake water, and is the first examination worldwide of seasonal trends in both concentrations and congener patterns.

I confirm that all co-authors have read and approve this version of the research paper, and care has been taken to ensure the integrity of the work.

The authors confirm that this is the original research work, and none piece of this manuscript has been published or is under consideration of publication elsewhere.

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Thanks for your time and the authors appreciate your consideration of this manuscript!

Kind regards

Yours sincerely,
Congqiao Yang

HIGHLIGHTS

- PBDE concentrations are comparable to those in the Great Lakes
- Σ BDE concentrations in water samples showed TSS dependence
- Σ BDE concentrations showed seasonal trends: higher in colder than in warmer periods
- Generally higher BDE-47:99 ratios in warmer than colder months
- BDE-47:99 ratios decreased significantly with increasing TSS content of samples

**Polybrominated diphenyl ethers (PBDEs) in English freshwater lakes,
2008-2012**

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ABSTRACT

Concentrations of tri-to-hexa-BDEs were determined in water samples taken from 9 English lakes on 13 occasions between April 2008 and February 2012. Across all sites, concentrations of Σ BDEs in individual samples ranged from 9.2 to 171.5 pg L^{-1} , with an average of 61.9 pg L^{-1} . Notwithstanding the far greater use of the Penta-BDE commercial formulation in the USA, concentrations in this study are comparable to the limited data available for the Great Lakes. PBDE concentrations showed no evidence of a decline at any monitored location over the study period. This may be because this study commenced 4 years after the introduction of restrictions on the Penta- and Octa-BDE formulations. While concentrations normalised to water volume at the different locations were statistically indistinguishable; significant spatial variation was apparent when the data were normalised to total suspended solids (TSS) content. However, this spatial variation was not correlated with factors such as population density and lake catchment area, suggesting that concentrations of PBDEs in lake water in this study are a complex integral of numerous factors. BDE-47:99 ratios and concentrations of Σ BDEs respectively decreased and increased significantly with increasing TSS content. As TSS content was elevated in colder compared with warmer periods, such seasonal variation in TSS content appears a major contributor to the observed elevation of Σ BDE concentrations in colder periods, and higher BDE-47:99 ratios in warmer periods.

Keywords: PBDEs; Lake Water; Temporal; Seasonal; Spatial; TSS

1. Introduction

Polybrominated diphenyl ethers (PBDEs) have been widely applied as brominated flame retardant (BFR) additives for several decades in many commercial products including plastics, rubbers, textiles, electronic components and building materials (Hale et al., 2006; Alaei et al., 2003). They are of great concern because of their ubiquitous presence and persistence in various environmental matrices, including biota, and their adverse effects in wildlife and humans (Hallgren and Darnerud, 2002; Branchi et al., 2003; Hardy, 2002; McDonald, 2002). Against this backdrop, the production and new use of the Penta-BDE and Octa-BDE formulations was phased out in Europe and North America in 2004 (Hale et al., 2006), with both listed in 2009 as Persistent Organic Pollutants (POPs) under the Stockholm Convention (SCOP, 2009). The United Kingdom consumed larger quantities of the Penta-BDE mixture than many other European countries (Kalantzi et al., 2004) and was the fourth largest PBDE producer in the world, with an annual output of ~25,000 t (Alaei et al., 2003). This production and use has had a demonstrable impact, exemplified by reports of the presence of PBDEs in UK human milk, air, soil, and sediment (Kalantzi et al., 2004; Harrad and Hunter, 2006; Vane et al., 2010).

Freshwater lakes provide important ecological, hydrological and societal services. However, studies of contamination of PBDEs in lake water are relatively scarce. As part of the Open Air Laboratories (OPAL) project, this study presents an investigation of the temporal/seasonal trends and spatial distribution of the concentrations of tri to hexa-BDEs (i.e. those predominant in the Penta-BDE formulation) in water from 9 freshwater lakes throughout England from April 2008 to February 2012. We believe that this study is only the second report - and the most comprehensive to date - of concentrations of PBDEs in European lake water, and is the first examination worldwide of seasonal trends in both concentrations and congener patterns. It

complements our previous report on concentrations of hexabromocyclododecanes (HBCDs) and tetrabromobisphenol-A (TBBP-A) in water, surficial sediment, and fish from the same lakes (Harrad et al., 2009). This study focuses on tri- through hexa-brominated PBDEs that are primarily found in the Penta-BDE commercial formulation. This reflects the fact that at the outset of this study, reliable analytical methods for the determination of BDE-209 (the major constituent of the Deca-BDE product) were not available in our laboratory.

The influence on PBDE concentrations and congener profiles of variables such as: total suspended solids (TSS) in water samples, population density, and proximity to landfill sites are examined, along with seasonal and temporal trends. As well as providing a valuable initial baseline against which future contamination trends can be compared; our data are analyzed to provide clues as to source attribution, and responses to recent restrictions on Penta-BDE use. Moreover, while UK production and use of Penta-BDE was substantial, it was dwarfed by that of the Americas which in 2001 (the most recent figures available) produced 7,100 t compared to 150 t in Europe (BSEF, 2006). We therefore compare our findings with recent reports of similar contamination in North America.

2. Materials and methods

2.1. Sampling strategy and methods

A map of the sampling locations is given as Figure 1, with more information about sampling locations supplied as supporting information (Table S1). Sampling was conducted on 13 occasions from each of 9 English freshwater lakes; however one sample for THOP was missing due to drought on one sampling occasion, and one sample was lost in analysis, making 115 samples in total. Between April 2008 to July 2010 inclusive, sampling frequency was quarterly, switching to biannually thereafter until the last sampling event in February 2012. At each

location, a grab sample of 40 L of bulk water was collected from the profundal point of each lake 50 cm below the surface in two x 20 L pre-cleaned HDPE containers. In November 2008, a surficial sediment sample was also collected from each site via procedures reported previously (Harrad et al., 2009).

2.2. Analytical protocols

2.2.1. Determination of PBDEs

Samples were filtered via gravity through a glass fibre filter (GFF, Whatman, UK, 12.5 cm diameter, 1 μm pore size), followed by two pre-cleaned polyurethane foam (PUF) plugs (8 cm diameter, 4 cm length, 0.03 g cm^{-3} each, PACS, Leicester, UK), with GFF and PUFs for each sample combined prior to soxhlet extraction for 8 h with dichloromethane, as described elsewhere (Harrad et al., 2009). For those samples taken in summer 2008, the filters and PUFs were analysed separately to provide information on the operationally defined particulate phase and dissolved phase. Freeze-dried surficial sediment samples (~1 g, accurately weighed) were mixed with 2 g Cu powder for removal of sulfur prior to pressurised liquid extraction as described previously (Harrad et al., 2009). Each sample was spiked prior to extraction with appropriate quantities of the following internal standards: $^{13}\text{C}_{12}$ -labeled BDE-28, -47, -99, and -153 (Greyhound Chromatography and Allied Chemicals, UK). Following extraction, crude extracts were concentrated and then subjected to florisil column (1 g) clean up. Analytes were eluted first with 15 mL hexane followed by 15 mL dichloromethane. The hexane and dichloromethane elutes were combined and extracted with dimethyl sulfoxide (DMSO) (3 x 10 mL). The DMSO extracts were pooled, diluted with 35 mL deionised distilled water and extracted sequentially with hexane (3 x 30 mL). The combined hexane extracts were then evaporated to incipient dryness under a stream of nitrogen (Turbovap). Final sample extracts were diluted in 50 μL hexane containing $^{13}\text{C}_{12}$ BDE-100 as a recovery determination standard

(RDS) and analysed for tri-hexa-BDEs via an Agilent 6850-5975 GC-MS operated in selective ion monitoring (SIM) mode, as reported elsewhere (Harrad and Hunter, 2006). Briefly, 1 μ L sample was injected with an auto-injector in splitless mode at 280°C. BDEs-17, -28, -49, -47, -66, -100, -99, -85, -154, and -153 were separated on a VF-5 ms capillary column (30 m x 0.25 mm x 0.25 μ m). The initial column temperature was 140°C held for 2 mins, ramped to 200 °C at 5 °C min⁻¹, then 300 °C at 2 °C min⁻¹ held for 5 mins, and 2 °C min⁻¹ to 310 °C. Ions monitored were: m/z 405.8 for BDE-17 and -28; m/z 485.8 for BDE-49, -47, and -66; m/z 403.8 for BDE-100, -99, and -85; m/z 483.8 for BDE-154 and -153. For surrogate (internal) standards, m/z 417.8, 497.8, 415.8, and 495.8 were monitored for ¹³C-BDE-28, -47, -99, and -153, respectively.

2.2.2. *Measurement of TSS*

To examine the relationship between PBDE concentrations and suspended particulate matter loadings, TSS content was determined gravimetrically via gravity filtration through a GFF in all samples using small aliquots of water (~1 L) collected from the same location at the same time specifically for TSS determination only (see Table S2 for TSS data). Given the uncertainty associated with TSS measurements acquired using these relatively small sample volumes (the ratio of TSS mass to the mass of the GFF ranged from 0.6-16.4% w/w); TSS was also determined gravimetrically before solvent extraction using the entire 40 L volume of the samples collected in February 2011.

2.3. *Method validation and QA/QC*

Method validation and accuracy were assessed via replicate (n=3) analysis of NIST standard reference material (SRM 2585), see Table S3 for details. These results reported RSD within 10% for all the BDE congeners. Obtained results compared favourably with the certified values. For

each batch of 9 samples, 2 blanks (each containing 2 pre-cleaned PUFs and 1 piece of GFF) were analysed. For the sediment samples, a sodium sulfate blank was analysed. PBDE concentrations in these blanks were either below method detection limits (ranging from 0.2-1.4 pg L⁻¹ for measured congeners), or revealed very trace and acceptable procedural contamination (less than around 5% of that in water samples). More information on QA/QC can be found in SI.

2.4. Statistical analyses

Statistical analyses were conducted using both Excel for descriptive statistics, with SPSS (IBM SPSS Statistics 21) used for ANOVA, correlation, regression, and t-test analyses.

3. Results

Concentrations of Σ BDEs in this study ranged from 9.2 to 171.5 pg L⁻¹ (see Table 1), with concentrations normalised to TSS also reported. By comparison, Stapleton and Baker (2001) reported that concentrations of PBDEs (BDE-47, -99, -100, -153, -154 and -183) in Lake Michigan increased from a mean value of 31 pg L⁻¹ in 1997 to 158 pg L⁻¹ in 1999. A later study reported that average concentrations of Σ BDEs (BDE-47, -66, -99, -100, -153 and -154; 2004) in Lake Michigan were 18 pg L⁻¹ and 3.1 pg L⁻¹ for the dissolved phase and particulate phase, respectively (Streets et al., 2006). Dissolved phase Σ BDE (BDE-47, -85, -99, -100, and -153) concentrations in Lake Winnipeg, Canada had a mean value of 29.5 pg L⁻¹, with BDE-47 the dominant congener (17.0 pg L⁻¹, n=6, 2004) (Law et al., 2006). By comparison, Σ BDE (BDE-47, -99, and -153) concentrations in an urban estuary in Narragansett were < 3 pg L⁻¹ (Sacks and Lohmann, 2012). Moreover, Σ BDE concentrations (same congeners as this study, except BDE-49) were 0.2 pg L⁻¹ to 299 pg L⁻¹ in San Francisco Bay water samples collected in July 2002, with BDE-47 dominant in most of the samples, followed by BDE-99 (Oros et al.,

2005). Oram et al. (2008) reported concentrations of BDE-47 in San Francisco Bay (2002-2006) to range from 15.5 to 337 pg L⁻¹ with a spatially unbiased mean value of 54.9 pg L⁻¹.

Outside North America, the Σ BDE (BDE-47, -99, and -153) concentration observed in a study of the Scheldt Estuary and North Sea along the Dutch coast was around 1.6 pg L⁻¹ (Booij et al., 2002), an order of magnitude lower than that observed in this study. More comparable with this study of freshwater lakes, mean concentrations of Σ BDE (BDE-28, -47, -99, -100, and -153) in 5 samples of water from Lake Thun in 2007, Switzerland were 36.4 pg L⁻¹; the only other data of which we are aware on PBDE concentrations in European lakes (Bogdal et al., 2010). Further afield, in the Zhujiang River estuary in China, concentrations of Σ BDEs (BDE-28, -47, -100, -99, -153, -154 and -183) were 26.1 to 94.6 pg L⁻¹ and 71.4 to 156.9 pg L⁻¹ in May and October, respectively (Luo et al., 2008). In summary, the concentrations reported in our study seem comparable and largely consistent with levels obtained elsewhere for various water bodies, except where samples were taken in heavily source-impacted areas. For instance, average Σ BDE concentrations (BDE-28, -47, -100, -99, -138, -153 and -154) in a reservoir at an e-waste recycling area in China were 21.8 ng L⁻¹ (Wu et al., 2008).

4. Discussion

4.1 PBDE concentrations: UK vs. USA

Interestingly, our data for English lakes is comparable with those reported for the USA (Streets et al., 2006; Sacks and Lohmann, 2012) in spite of the far greater production of the Penta-BDE product in the Americas than Europe. While this contrasts with the higher PBDE concentrations observed in North American house dust compared to the UK (Harrad et al., 2008), it is consistent with similar concentrations of PBDEs in outdoor air in the USA and the UK (Harrad and Hunter., 2006). The cause(s) of these somewhat conflicting observations are

not clear at this time, but we note that the UK has a substantially higher population density than the US, which means the Penta-BDE usage in the UK and the USA may actually be similar when normalised to surface area.

4.2. Partitioning of PBDEs between dissolved and particulate phase

Table S4 reports the Σ BDE concentrations determined in the particulate and freely dissolved phases separately in the July 2008 samples; the latter operationally defined as that passing through a 1 μ m pore size GFF, to provide information on relative abundances of the PBDE concentrations in each phase. Across all sites, 62-77% of Σ BDE was found in the particulate phase, with an average $\pm\sigma_n$ value of $68\pm6\%$. Oros et al. (2005) reported the phase partitioning of Σ BDEs (sum of 22 tri- through decabrominated congeners) in water samples (n=3) from the San Francisco estuary, finding 78% to 93% of Σ BDEs present in the particulate phase using an identical 1 μ m cut-off to that used in this study. This is generally consistent with our findings, particularly given the inclusion of BDE-209 in the San Francisco study.

4.3. Factors influencing PBDE concentrations

4.3.1 Influence of TSS on PBDE concentrations

The TSS content of samples collected from all sites in February 2011 was determined gravimetrically after filtration of the entire 40 L sample. Values ranged from 0.32 mg L⁻¹ at HOLT to 46 mg L⁻¹ at PFLE. As shown in Figure 2(a), the Σ BDE concentrations showed some dependence on TSS ($r^2=0.2135$, blue line), that was enhanced significantly when the PFLE site was excluded (green line, $r^2=0.7619$, $P<0.01$). Those strong correlations demonstrate clearly the influence of TSS on PBDE contamination. Moreover, TSS contents determined for all samples (using smaller volumes and likely subject to greater uncertainty) also showed positive correlation with Σ BDE concentrations ($r^2=0.036$, $p<0.05$). With respect to the PFLE site,

although it exhibited PBDE concentrations at the higher end of those recorded in this study, the concentrations recorded at this site were lower than expected given the high TSS content of samples from PFLE. This site is known to occasionally suffer episodes of cyanobacteria (blue-green) algae in summer. Sugiura (1992) reported microbial degradation of PCBs on suspended particulates in aquatic environments. Moreover, microbial transformation of PBDEs in marine sediments was confirmed by Martin et al. (2004). While recognising that more detailed study is required to verify this, we therefore hypothesise that the occasional episodes of cyanobacteria at PFLE may have enhanced PBDE degradation, thereby reducing the correlation between TSS and PBDE concentrations at this site. Inclusion of TSS data along with season (warmer periods from March 21st to September 20th were defined as 1 while colder periods from September 21st to March 20th were defined as 2) in linear regression analysis revealed significant correlations between both parameters and Σ BDE.

$$\Sigma\text{BDE} = 17.844 \text{ season} + 0.53 \text{ TSS} + 30.893; r^2 = 0.133, p < 0.05; \beta = 0.313 \text{ for season and } \beta = 0.222 \text{ for TSS} \quad (1)$$

This indicates that Σ BDE concentrations were higher in colder months and at higher TSS values. Our findings are consistent with those of Oros et al. (2005), who reported a significant positive relationship between Σ BDE concentrations and TSS in the San Francisco estuary.

4.3.2 Seasonal impacts on PBDE concentrations

As indicated by regression equation (1), PBDE concentrations at all sites were elevated in colder compared to warmer periods (see Figure 3), with average water temperatures of 6.4 °C and 16.4 °C across 9 lakes in the two periods, respectively. The higher β value for season ($\beta = 0.313$) than for TSS ($\beta = 0.222$) suggests the former to exert a slightly stronger influence on

PBDE contamination levels. Data on PBDE seasonal trends in water bodies with which to compare our data are extremely scarce. Luo et al. (2008) reported that PBDE concentrations in water from the Zhujiang River Estuary varied seasonally being lower in May 2005 than October of that year. However, in this instance, rather than water temperature, the cause was attributed to the fact that in May brackish water was dominant in the estuary, as opposed to the situation in October when fresh water from river runoff, which was indicated to be the major contributor of PBDEs into the Estuary, was dominant. Moreover, there is conflicting information about seasonal trends of PCB contamination in water bodies. Dissolved phase concentrations of PCBs showed no seasonal trends in the Hudson River Estuary from December 1999 to April 2001 (Yan et al., 2008), nor across Baltimore Harbour and the Northern Chesapeake Bay in 1996-97 (Bamford et al., 2002). Consistent with our observations however, maximum PCB concentrations associated with TSS in water from the Seine Estuary were observed in winter over the period November 2002 to February 2005 (Cailleaud et al., 2007).

In line with this study in the Seine for PCBs (but reported here for PBDEs for the first time), we observed higher TSS contents in colder compared to warmer periods at CRAZ, EDGB, HOLT, MARM, and THOP (by factors of 1.12, 1.83, 1.33, 1.41, and 2.27, respectively). Such winter increments in TSS are likely attributable to greater re-suspension of sediment due to die-back of aquatic plants and increased mixing of the water column due to higher precipitation and wind speeds during colder periods. The increases in TSS corresponded with similar increments in average Σ BDE concentrations at the same sites in colder compared to warmer periods (factors of 1.14, 1.52, 1.08, 1.34, and 2.38, respectively). For these 5 sites therefore, the winter increment in Σ BDE contamination appears at least partly attributable to seasonal variations in TSS content. This is confirmed by the observation that while seasonal trends in

TSS-normalised PBDE concentrations were apparent; they were generally weaker than for the un-normalised data with significantly higher concentrations in colder periods observed for only 6 out of 9 lakes (Fig. 4). In addition to seasonal variation in TSS content therefore, we hypothesize that another likely explanation for our observed winter peak in Σ BDE concentrations is that lower water temperatures will reduce the extent of PBDE volatilization. Another possible contributory factor is that the rate of any PBDE degradation will be slower at lower temperatures. Both of these factors favour higher PBDE concentrations when water temperatures are lower.

4.3.3 Temporal trends in PBDE concentrations

There was no evidence for any significant temporal trend in PBDE concentrations (whether water volume-based or TSS-normalised) at any of our 9 lakes over the 4 year monitoring period of this study. This is in contrast with recent observations of declining atmospheric concentrations. Specifically, European background airborne PBDE concentrations (BDEs -28, -47, -49, -99, -100, -153, -154, and -183) were reported to have declined with a half-life of 2.2 ± 0.4 years between 2000 and 2008 (Schuster et al., 2010). Likewise, concentrations in air of a similar range of PBDEs were reported to be declining during the 2000s at 3 out of 4 UK monitoring locations with average half-lives between 2.0 and 3.5 years (Birgul et al., 2012). Despite such evidence from the atmosphere of encouraging responses to the recent restrictions on use of PBDEs in the EU; the absence of any decline on concentrations in lake water in our study is not surprising given the four year duration of our study, the lack of any known direct point sources of PBDEs to our lakes, and the comparatively long mixing times of freshwater lakes in general that exceed those of the atmosphere. It is also possible that any decline in PBDE concentrations at our lakes was rapid following the restrictions on PBDE manufacture and use, and had thus occurred before our study commenced. We also note that no decline in

atmospheric PBDE concentrations was observed at one of the two UK rural sites monitored by Birgul et al. (2012). Further longer-term monitoring is therefore required to elucidate the impact on the lacustrine environment of restrictions on manufacture and use of PBDEs within the EU.

4.3.4 Spatial trends in PBDE concentrations

As TSS content was shown above to influence PBDE concentrations; we also investigated spatial trends in PBDE concentrations when normalised to TSS content. While no spatial trends were apparent in PBDE concentrations expressed on a water volume basis; significant inter-site variability was observed when PBDE concentrations were normalised for TSS content (ANOVA, $p < 0.01$), with the highest and lowest concentrations at HOLT and PFLE, respectively. This suggests that location does influence the PBDE concentrations observed in our lakes. We investigated possible causes of this spatial variation via multi-linear regression of TSS-normalised concentrations against factors such as: lake area, mean depth, lake catchment area, lake catchment ratio (defined as the ratio of lake area to catchment area), lake altitude, and the population density of both: (a) the local authority within which each site was located; and (b) the local authorities within a 25 km radius of each site. No significant relationships were detected, with the same lack of correlation observed also when water-volume based PBDE concentrations were used as the dependent variable. These findings likely reflect the fact that PBDE concentrations in water in the lakes in this study are a complex integral of many influential factors.

4.4 Congener profile of PBDEs

The major congeners detected in all 115 samples were BDE-99 and BDE-47. BDE-99 was the dominant congener at most sites with average BDE-47:99 ratios of 0.91, 0.66, 0.59, 0.92, 0.95

and 0.73 at CRAZ, EDGB, HOLT, PFLE, THOP and WAKE respectively. However average BDE-47:99 ratios of 1.01, 1.02 and 1.08 were observed at CHAP, MARM and SLT, respectively. The BDE-47:99 ratio in a given matrix is a complex integral of the ratio in the initial source (~0.79-0.96 in Penta-BDE formulations; La et al., 2006), and the comparative environmental fate of the two congeners following emission. The latter is governed by their physicochemical properties, e.g. one would hypothesize greater partitioning to air for the more volatile BDE-47, while BDE-99 would partition preferentially to soil and sediment due to its higher K_{OA} and K_{OW} (Palm et al., 2002). This is consistent with previous studies reporting BDE-47:99 ratios in soil at 10 UK locations of between 0.51 and 0.88, while in outdoor air collected at the same 10 UK locations, BDE-47:99 ratios varied between 2.95 and 3.62 (Harrad and Hunter, 2006). A paired t-test comparing average BDE-47:99 ratios in water samples for each site over all 13 sampling events, with those determined in surficial sediment taken in November 2008 at the same sites (see Table S5), showed BDE-47:99 ratios were significantly higher ($p < 0.01$) in water (0.75 to 1.33 with average value of 1.09) than in surficial sediment (0.29 to 1.16 with average value of 0.62). We hypothesise that the higher K_{OW} of BDE-99 leads to greater partitioning to surficial sediment than water, and thus lower BDE-47:99 ratios in sediment.

In comparison to our study, BDE-47 dominated most of the samples in San Francisco Bay, followed by BDE-99 (Oros et al., 2005). The higher abundance of BDE-99 in our study may be due to a number of factors. These include: differences in PBDE environmental fate and behaviour between estuarine/marine waters and freshwaters, e.g. higher NaCl concentrations in marine/estuarine water would “salt-out” the more lipophilic BDE-99 to surficial sediment; possible international differences in the congener profile of the Penta-BDE formulation used; varying transfer distances between source and sampling site which may alter the relative

abundance of different congeners, and/or greater environmental persistence of BDE-99 relative to BDE-47 following recent restrictions on the manufacture and use of Penta-BDE. This latter hypothesis is plausible given the fact that the Penta-BDE formulation was restricted earlier in Europe than in the USA. Moreover, variations in the TSS content of the samples in different studies may play a role. Further to our observations of the important influence of TSS on PBDE concentrations, we also detected a decrease of BDE-47:99 ratios with increasing TSS content in the February 2011 samples for which TSS measurements were made using the entire 40 L sample, as shown in Figure 2(b). We believe this is a result of the stronger partitioning to suspended sediment of BDE-99 relative to BDE-47, driven by its higher K_{OC} . To our knowledge, this is the first report of a relationship between BDE-47:99 ratios and TSS in water samples.

We also detected that at 7 of the 9 sampling sites, BDE-47:99 ratios displayed intra-site fluctuation with generally higher ratios observed in samples taken in warmer sampling months (July) than in colder months (January and February). To our knowledge, this is the first report of such seasonal variation in congener patterns of PBDEs in freshwater lakes. The average BDE-47:99 ratios in warmer periods exceed that in colder seasons by a factor of 1.48 across 13 sampling occasions. We examined the influence of season on our BDE-47:99 ratios further using linear regression and again defining warmer periods as 1 and colder periods as 2. Defined thus, season showed a statistically significant negative linear relationship with BDE-47:99 ratios across all 115 water samples.

$$\text{BDE-47:99} = -0.414 \text{ season} + 1.689; (r^2=0.078, p<0.01) \quad (2)$$

In addition, BDE-47:99 ratios across all samples showed some dependence on water temperature (see Table S6 for information) measured 50 cm below the surface at the time of each sampling event with a regression linear equation of:

$$\text{BDE-47:99} = 0.032 \text{ temperature} + 0.711; (r^2 = 0.068, p < 0.01) \quad (3)$$

Interestingly, when each site is examined individually, this seasonal trend in 47:99 ratios was not significant in the first two years of monitoring, but was highly significant in the second half of the monitoring period. Longer term monitoring is required to determine whether seasonal variations in congener profiles are genuine. However, this seasonal variation is consistent with the abovementioned inverse relationship between TSS and BDE-47:99 ratios and our observation of higher TSS in colder periods. Additionally, we suggest that higher BDE-47:99 ratios in warmer than in colder periods may also be due to the fact that in warmer periods one would expect preferential degassing from sediment of the more volatile BDE-47, and enhanced temperature-driven partitioning of BDE-99 to sediment organic carbon in winter.

5. Conclusions

Based on the very limited data available, PBDE contamination levels in English freshwater lakes were comparable to those in the Great Lakes. Despite being phased out in 2004, no temporal trends were observed over the period 2008-2012. When normalised for TSS content, PBDE concentrations showed significant inter-site variability, but no relationship was found between this spatial variability and factors such as population density and catchment area. Seasonal trends were observed, with higher PBDE concentrations in colder than in warmer periods, and higher BDE-47:99 ratios in warmer months. These seasonal trends are in part attributable to the increased TSS concentrations in colder compared to warmer months.

388

389 **Appendix: Supplementary materials**

390 Tables containing information on: sampling locations, TSS content and temperature of water
391 samples, QA/QC data, ΣBDE concentrations in operationally-defined particulate and dissolved
392 phases, as well as a comparison of BDE-47:99 ratios in water and surficial sediment samples.

393

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400

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Table 1: Concentrations of ΣBDEs^a in water expressed on both a water volume (pg L⁻¹) and TSS normalised basis (pg mg⁻¹, in parentheses)
in English lakes

<div>Date</div> <div>Location</div>	Apr/08	Jul/08	Nov/08	Jan/09	Apr/09	Jul/09	Oct/09	Jan/10	Apr/10	Jul/10	Feb/11	Jul/11	Feb/12	Average Concentration ±σ _n
Chapman’s Pond (CHAP)	16.9 (2.0)	74.4 (7.1)	74.0 (10.9)	71.6 (19.9)	70.7 (8.8)	87.2 (6.4)	65.1 (4.7)	64.3 (11.6)	74.9 (5.5)	55.3 (5.4)	22.3 (2.5)	14.8 (1.1)	61.7 (33.3)	57.9±24 (9.2±8.8)
Crag Lough (CRAZ)	20.8 (7.4)	70.0 (21.5)	72.1 (10.2)	82.6 (23.6)	66.1 (73.4)	83.4 (22.5)	78.9 (56.3)	87.0 (67.0)	73.0 (36.5)	141.5 (11.0)	59.2 (4.4)	9.2 (1.9)	75.4 (30.8)	70.7±32 (28.2±23.8)
Edgbaston Pool (EDGB)	14.5 (19.3)	57.1 (14.1)	62.7 (9.5)	72.8 (16.8)	65.8 (7.2)	51.0 (25.5)	53.9 (39.9)	60.5 (11.1)	86.7 (31.5)	47.0 (14.9)	39.4 (5.1)	13.7 (4.3)	149.1 (10.8)	59.6±34 (16.2±10.6)
Holt Hall Lake (HOLT)	28.5 (49.1)	59.5 (99.1)	57.5 (34.8)	68.3 (30.8)	63.0 (45.0)	67.1 (40.6)	72.0 (35.1)	79.5 (45.4)	66.5 (57.9)	52.8 (36.4)	28.6 (26.0)	48.5 (19.0)	52.9 (27.9)	57.3±15 (42.1±20.0)
Marton Mere (MARM)	17.3 (15.1)	42.4 (10.9)	44.0 (14.9)	56.6 (24.1)	47.2 (17.8)	56.4 (40.3)	59.8 (37.4)	71.5 (13.5)	55.9 (27.3)	59.4 (10.0)	90.7 (10.5)	55.3 (42.6)	61.3 (42.3)	55.2±17 (23.6±12.9)
Fleet (PFLE)	16.0 (0.5)	61.0 (1.2)	72.9 (3.4)	88.8 (4.1)	79.3 (1.6)	88.8 (1.7)	69.6 (3.5)	86.6 (4.6)	110.1 (2.8)	71.6 (1.2)	83.5 (1.6)	48.3 (1.2)	72.9 (8.4)	73.0±23 (2.8±2.1)
Slapton (SLT)	41.9 (18.7)	60.2 (7.3)	56.2 (74.9)	64.9 (8.7)	56.5 (32.3)	69.1 (19.5)	132.7 (89.3)	90.7 (31.8)	85.2 (20.3)	85.4 (3.0)	31.1 (5.1)	24.4 (1.3)	90.3 (30.1)	68.4±29 (26.3±27.1)
Thoresby Lake (THOP)	15.0 (0.7)	44.2 (35.4)	49.7 (2.9)	56.8 (4.1)	56.0 (6.2)	60.9 (58.0)	- (24.0)	122.2 (24.0)	- (35.7)	73.3 (35.7)	171.5 (9.0)	21.3 (14.2)	136.0 (12.7)	73.3±49 (18.4±18.0)
Wake Valley Pond (WAKE)	33.0 (6.3)	45.0 (4.0)	41.6 (4.3)	45.9 (10.4)	40.3 (10.5)	46.5 (17.9)	53.4 (15.3)	59.2 (20.4)	52.4 (10.9)	38.0 (10.9)	17.7 (3.8)	13.8 (3.0)	52.7 (11.3)	41.5±13 (9.9±5.6)

^a Sum of BDE-17, -28, -49, -47, -66, -100, -99, -85, -154, and -153

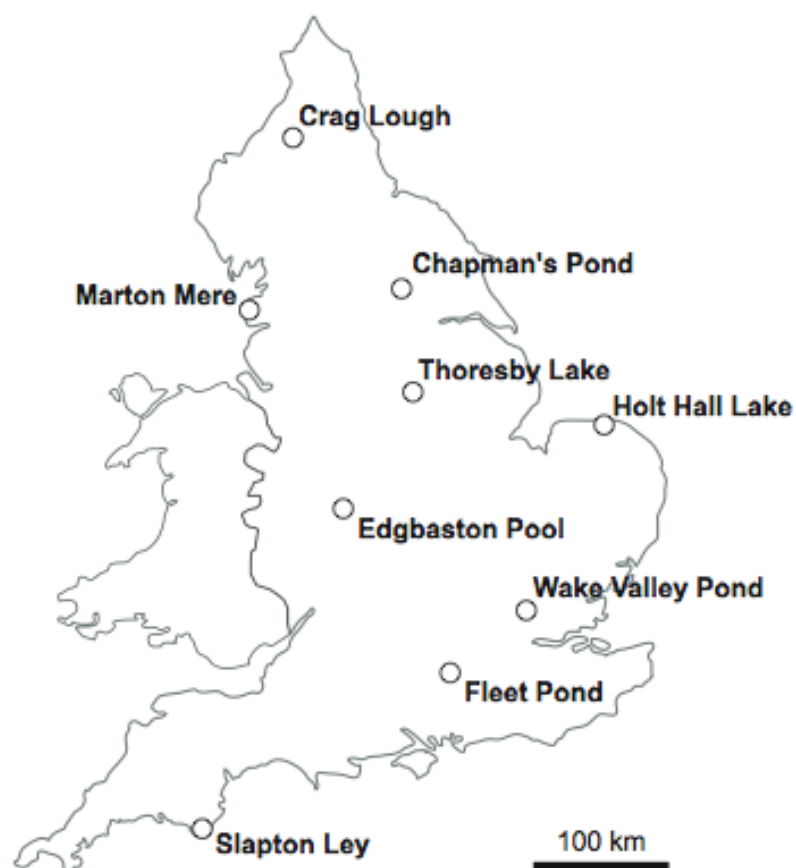


Fig. 1. Location of sampling sites

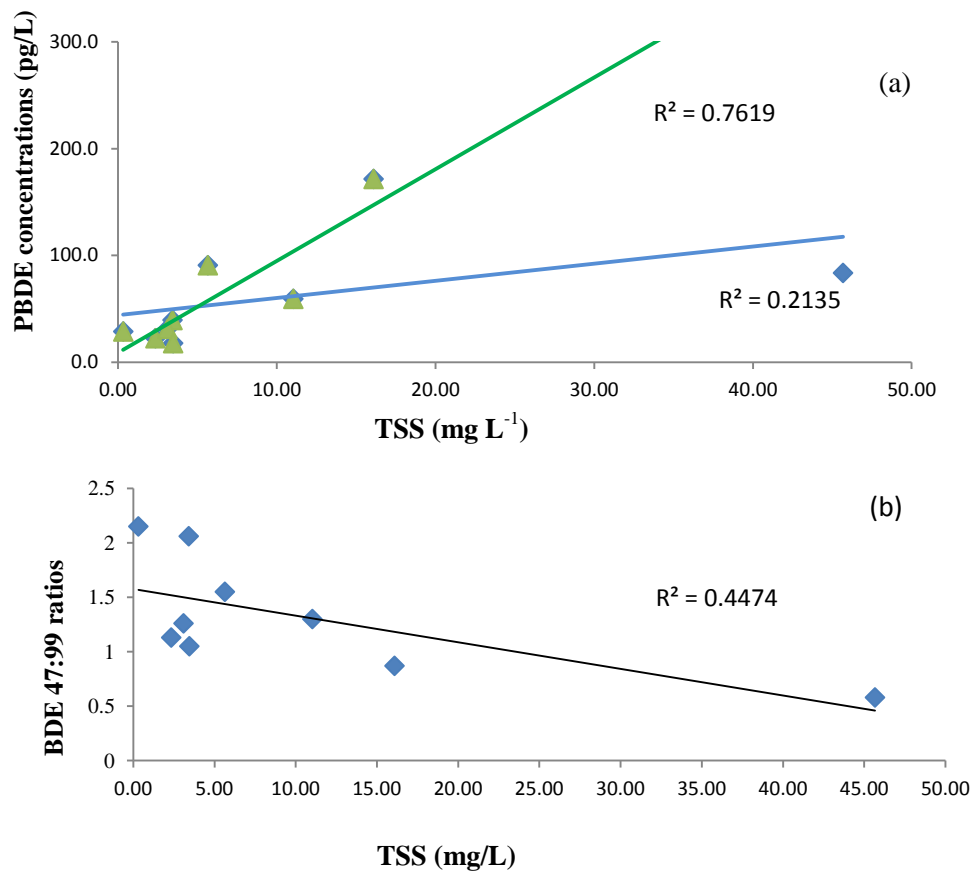


Fig. 2. Correlations between TSS content (measured for February 2011 samples only) and PBDE concentrations (a) (with and without PFLE sites, blue and green lines, respectively) and (b) BDE-47:99 ratios

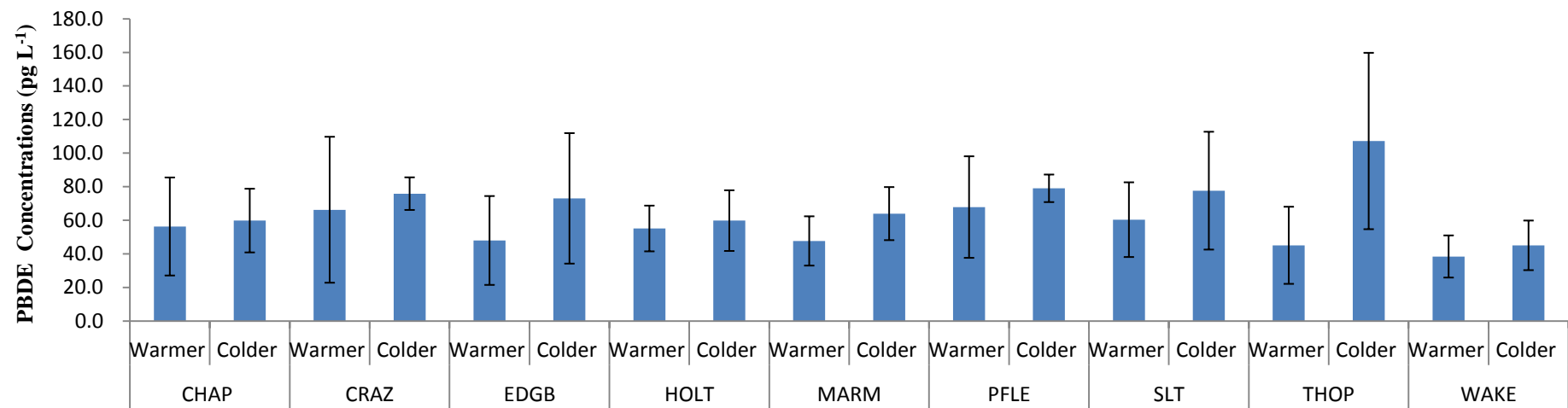


Fig. 3. Average PBDE concentrations (with standard deviation as y-error bar) in warmer and colder periods in individual lakes, April 2008 to February 2012

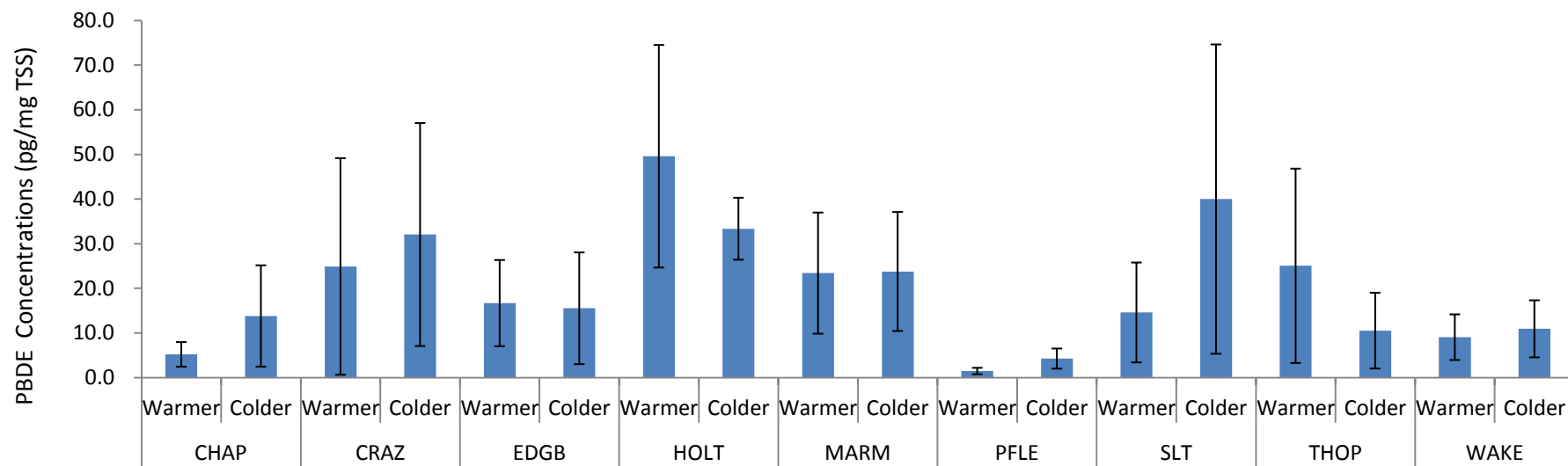


Fig. 4. Average TSS normalised PBDE concentrations (with standard deviation as y-error bar) in warmer and colder periods in individual lakes, April 2008 to February 2012

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